

# Dissipative particle dynamics with energy conservation: equilibrium properties

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## Abstract

The stochastic differential equations for a model of dissipative particle dynamics, with both total energy and total momentum conservation at every time-step, are presented. The algorithm satisfies *detailed balance* as well as the *fluctuation-dissipation* theorems that ensure that the proper thermodynamic equilibrium can be reached. Macroscopic equilibrium probability distributions as well as *equations of state* for the model are also derived, and an appropriate definition of the free energy of the system is consistently proposed. Several simulations results of equilibrium as well as transport properties, including heat transport and thermal convection in a box, are shown as proof of the internal consistency of the model.

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# 1 Introduction

The computer simulation strategy for dynamics of complex systems known as *Dissipative Particle Dynamics* or, simply, DPD, has been the subject of several studies in recent years. This methodology was introduced by Hoogerbrugge *et al.*[1] to model the dynamic behaviour of fluids by using a particulate method in which an ensemble of *mesoscopic* particles interact with each other via conservative as well as dissipative forces. Contrary to other particulate *Lagrangian* methods[2], oriented at modelling the hydrodynamics of macroscopic systems, DPD also incorporates Brownian forces in the particle-particle interactions. In this way, thermal fluctuations can be described and a certain thermodynamic equilibrium exists. DPD is, therefore, especially suited to the modelling of mesoscopic systems, where fluctuations play an important role. One can mention, for instance, the dynamics of polymer solutions, nucleation and phase separation problems, dynamics of confined fluids, colloidal suspensions, and kinetics of chemical reactions in confined geometries, etc. The DPD method has already been successfully applied to some cases of practical interest such as to the rheology of colloidal suspensions[7] and to the microphase separation of diblock copolymer solutions[8], among others.

In DPD, dissipative and random interactions are pairwise and chosen in such a way that the center of mass motion of each interacting pair is insensitive to these frictional and random forces. Hence, on the one hand, if closed and thermally isolated, the system relaxes fast to its thermal equilibrium and, on the other, its overall momentum is a conserved variable in view of the particle's momentum exchange rules. This second feature allows the system to exhibit a hydrodynamic behaviour from a macroscopic point of view, that is, for length and time scales larger than those characterizing the particle-particle interactions. With respect to other mesoscopic models for hydrodynamic behaviour such as Lattice Gas[3] or Cellular Automata[4], the DPD model is isotropic and Galilean-invariant due to the fact that it is not defined on a lattice and is straightforwardly based on Newton's equations of motion, as in MD. In addition, it has no extra conservation laws and is also computationally

efficient. As originally formulated, however, the DPD model can only deal with isothermal conditions since dissipative and Brownian forces cause no energy conservation in the particle-particle interaction. The equation for the energy transport is then of the relaxation type[6] and, therefore, heat flow, related to the energy conservation at the microscopic scale, cannot be described within the framework of the original model (which will be referred to as isothermal DPD from now on). In many problems of interest, either fundamental or applied, the study of the transport properties of heat at the mesoscopic level are very important. Thus, the incorporation of the thermal effects into a DPD algorithm is necessary for future applications of the method to problems of relevance.

In a previous paper[18] we introduced an algorithm in which the conservation of the total energy in the particle-particle interaction was consistently taken into account with the inclusion of the particle's internal energy in the model (this model will be referred to as DPDE from now on). In this paper we will analyze several aspects of this novel DPDE algorithm. In the first place, we discuss the extension of our original algorithm, given in ref.[18], to incorporate, on the one hand, temperature dependencies in the dynamic parameters of the model so that the treatment of arbitrary temperature-dependencies in the transport coefficients can be treated, something lacking in the older DPD models. On the other hand, we develop a direct derivation of the algorithm from the Langevin equations of motion for the relevant variables, by introducing a interpretation rule for these Langevin equations that ensures that the detailed balance condition is satisfied in an Euler-like algorithm. The detailed balance condition is necessary for the system to evolve towards the proper thermodynamic equilibrium. Furthermore, the algorithm obtained in this way conserves the energy at *every time-step* instead of *in the mean* as was the case in the older DPDE algorithm[18]. We have noticed that different algorithms lead to the same Fokker-Planck equation, i.e., different stochastic processes can lead, in fact, to the same dynamics for the probability distribution. In the second place, we have analyzed the macroscopic equilibrium properties of the DPDE system. We have shown that a thermodynamic analysis of the DPDE system is possible in view

of the fact that the equilibrium probability distribution is known. Properties such as a free energy or the equations of state can be derived in terms of the parameters defining the model. The simulation results of the equilibrium properties show an excellent agreement with the theoretical predictions. Third and last, we have done simulations in systems under a temperature gradient imposed by the temperature of two walls. We have found temperature profiles, as expected since the model allows the simulation of heat transport, and the existence of inhomogeneous temperature distributions, which is one of the main virtues of the DPDE algorithm. Furthermore, if a gravity field is considered, the system undergoes convective motion in addition to the temperature gradient, the Rayleigh number qualitatively estimated as being of the order of  $10^3$ .

The paper is organized as follows. In section II, we introduce the main hypothesis underlying the formulation of the DPDE model[18], and derive the appropriate algorithm with arbitrary dependence of the transport coefficients with the temperature, and energy conservation at every time-step. The Fokker-Planck equation describing the evolution of the probability distribution for the ensemble of variables describing the state of the system is also derived together with the corresponding fluctuation-dissipation theorems. In section III, we obtain the macroscopic equilibrium properties of the DPDE model and expressions for the equations of state and thermodynamic properties. At the end of this section, we pay attention to a particular model, used to perform simulations of equilibrium properties as well as heat transport and thermal convection. Finally, in section IV we draw the main conclusions from our work.

## 2 Dissipative particles with energy conservation

For our purposes, it is useful to have a physical picture and regard the dissipative particles as if they were *clusters* of true physical particles[5, 6], i.e., as particles with internal structure bearing some degrees of freedom. Thus, the DPDE model is

mesoscopic in nature since it resolves only the overall center-of-mass motion of the cluster and ignores the exact *internal state* of the cluster as a relevant variable. The interactions being dissipative and random, however, the total energy of the system is not conserved unless the energy exchanged between the resolved degrees of freedom and the internal state of the DPD particle is accounted for. We propose here a model based on the treatment of thermodynamic and hydrodynamic fluctuations[13, 10, 11], to consistently take into account the energy stored in the internal degrees of freedom of each particle, without explicit consideration of any *internal* Hamiltonian.

## 2.1 Definition of the model

Our model is based on the following assumptions:

1. The system contains  $N$  particles interacting with each other via conservative as well as dissipative interactions. The conservative interactions are described by the Hamiltonian

$$H(\{\vec{r}_i\}, \{\vec{p}_i\}) \equiv \sum_i^N \left\{ \frac{p_i^2}{2m} + \sum_{j>i} \psi(r_{ij}) + \psi^{ext}(\vec{r}_i) \right\} \quad (2.1)$$

where  $r_{ij} \equiv |\vec{r}_i - \vec{r}_j|$ . The Hamiltonian depends on the momenta and the positions of all the particles. The particles interact through pair potentials  $\psi(|\vec{r}_i - \vec{r}_j|)$ , depending only on the distance between them, and with an external field  $\psi^{ext}(\vec{r}_i)$

2. In addition, the particles can store energy in some internal degrees of freedom. The internal energy  $u_i$ , with  $u_i \geq 0$ , is introduced as a new relevant coordinate. The momentum  $\vec{p}_i$ , the position  $\vec{r}_i$  together with the internal energy  $u_i$ , completely specify the state of the dissipative particle at a given instant  $t$ .
3. The particle-particle interaction is pairwise and conserves the total momentum and the total energy when the internal energy of the pair is taken into account.

4. The internal states of the particle have no dynamics in the sense that they are always in equilibrium with themselves. This allows us to define a function  $s_i(u_i)$ . This function can arbitrarily be chosen according to the user's needs, except that it is constrained to thermodynamic consistency requirements[13]

(a)  $s_i$  must be a differentiable monotonically increasing function of its variable  $u_i$ , so that  $u_i(s_i)$  exists and  $\theta_i \equiv \partial u_i / \partial s_i$  exists and is always positive.

(b)  $s_i$  is a concave function of its argument.

Defined in this way,  $s_i$  can be viewed as a mesoscopic *entropy* of the  $i^{th}$  particle, and  $\theta_i$  can be seen as the particle's *temperature*. The change in  $u_i$  and in  $s_i$  are related by a Gibbs equation

$$\theta_i ds_i = du_i, \text{ which implies } \theta_i \dot{s}_i = \dot{u}_i \quad (2.2)$$

where the dot over the variables is used to denote time-differentiation from now on.

5. The irreversible particle-particle interaction is such that the deterministic part (in the absence of random forces) must satisfy

$$\dot{s}_i + \dot{s}_j \geq 0 \quad (2.3)$$

where  $i$  and  $j$  label an arbitrary pair of interacting particles.

6.  $u_i$ ,  $s_i$  and  $\theta_i$  must remain unchanged under a Galilean transformation, so that these variables are true scalars.
7. The equilibrium probability distribution for the relevant variables of the system under isothermal conditions is chosen to be

$$P_e(\{\vec{r}_i\}, \{\vec{p}_i\}, \{u_i\}) \sim e^{-H(\{\vec{r}_i\}, \{\vec{p}_i\})/kT} \prod_i e^{s_i(u_i)/k - u_i/kT} \quad (2.4)$$

where  $k$  is Boltzmann's constant and  $T$  is the thermodynamic, i.e., macroscopic temperature. The first factor on the right hand side of eq. (2.4) contains the probability distribution for the set of variables  $\{\vec{r}_i\}, \{\vec{p}_i\}$ , as given

by equilibrium statistical mechanics. The second factor on the right hand side corresponds, in turn, to the probability distribution for the internal energy of the particles as obtained from equilibrium fluctuation theory[13]. Effectively,  $\exp(s_i(u_i)/k - u_i/kT)$  gives the probability for the  $i^{th}$  particle to have an internal energy  $u_i$  regarding the rest of the system as a heat reservoir. The maximum of  $s_i(u_i)/k - u_i/kT$  occurs at  $\theta_i = T$ , in agreement with our interpretation of  $\theta_i$  as the particle's temperature. Furthermore, notice that

$$\left\langle \frac{1}{\theta_i} \right\rangle = \frac{1}{\mathcal{N}} \int du_i e^{(s_i(u_i)/k - u_i/kT)} \frac{\partial s_i}{\partial u_i} = \frac{1}{T} \quad (2.5)$$

where  $\mathcal{N}$  is the normalisation constant. Once the equilibrium probability distribution is obtained, the *thermodynamic* properties of the model are determined.

## 2.2 Dynamics of the model

The model defined so far must be completed with a set of equations that explicitly establish its dynamical properties. Initially, in view of the pairwise additivity of the interactions, we will analyze an arbitrary pair of particles,  $i$  and  $j$  say, and later on give the complete expressions for the  $N$ -particle system.

The change in position and momentum of the  $i^{th}$  particle due to the interaction with the  $j^{th}$  particle follows from Newton's second law

$$\dot{\vec{r}}_i = \frac{\vec{p}_i}{m} \quad (2.6)$$

$$\dot{\vec{p}}_i = \vec{F}_{ij}^C + \vec{F}_i^{ext} + \vec{F}_{ij}^D + \vec{F}_{ij}^R \quad (2.7)$$

where  $\vec{F}_{ij}^C \equiv -\partial\psi(r_{ij})/\partial\vec{r}_i$  and  $\vec{F}_i^{ext} \equiv -\partial\psi^{ext}(\vec{r}_i)/\partial\vec{r}_i$  are the forces due to the conservative interactions.  $\vec{F}_{ij}^C$  is, by construction, directed along the vector  $\hat{r}_{ij} \equiv (\vec{r}_j - \vec{r}_i)/r_{ij}$  and satisfies  $\vec{F}_{ij}^C = -\vec{F}_{ji}^C$ . In addition,  $\vec{F}_{ij}^D$  stands for the dissipative particle-particle interaction force and  $\vec{F}_{ij}^R$  is the random force associated with the former. The total energy  $e_i$  of the  $i^{th}$  particle is the sum of the kinetic ( $p_i^2/2m$ ), the potential ( $\psi(r_{ij})/2 + \psi^{ext}(\vec{r}_i)$ ), and the internal energy ( $u_i$ ) contributions. Using eq.

(2.7) to compute the change in the kinetic energy, we arrive at the equation for the change in the total energy

$$\dot{e}_i = \frac{d}{dt} \frac{p_i^2}{2m} + \frac{d}{dt} \left( \frac{1}{2} \psi(r_{ij}) + \psi^{ext}(\vec{r}_i) \right) + \dot{u}_i = \frac{1}{m} \vec{p}_i \cdot (\vec{F}_{ij}^D + \vec{F}_{ij}^R) + \frac{1}{2m} (\vec{p}_i + \vec{p}_j) \cdot \vec{F}_{ij}^C + \dot{u}_i. \quad (2.8)$$

The conservation of the total momentum of the pair imposes that its change is only due to the action of external force fields, that is,

$$\dot{\vec{p}}_i + \dot{\vec{p}}_j = \vec{F}_i^{ext} + \vec{F}_j^{ext}, \quad (2.9)$$

Therefore, we must have that  $\vec{F}_{ij}^{D,R} = -\vec{F}_{ji}^{D,R}$ . In addition, conservation of the total angular momentum

$$\vec{r}_i \times \dot{\vec{p}}_i + \vec{r}_j \times \dot{\vec{p}}_j = \vec{r}_i \times \vec{F}_i^{ext} + \vec{r}_j \times \vec{F}_j^{ext} \quad (2.10)$$

implies that dissipative as well as Brownian forces,  $\vec{F}_{ij}^{D,R}$ , must be directed along the unit vector  $\hat{r}_{ij}$ . Conservation of the total energy in the particle-particle interaction,  $\dot{e}_i + \dot{e}_j = 0$  gives, in turn, the rate of change of the internal energy of the pair

$$\dot{u}_i + \dot{u}_j = -\frac{1}{m} (\vec{p}_i - \vec{p}_j) \cdot (\vec{F}_{ij}^D + \vec{F}_{ij}^R) \quad (2.11)$$

This equation implies that if the total energy is to be conserved, then the change in the total internal energy has to be due to the work done by the dissipative and the associated random forces. The dissipative forces transfer mechanical energy to internal energy, while random forces bring back internal energy to the kinetic and potential energies of the particles. From the conservation equations alone, however, nothing can be inferred about how the internal energy is distributed among the particles so that one has to supply a given model.

We will assume that the mechanisms driving the change in the internal energy of the particles are of two kinds. On the one hand, the work done by dissipative and random forces is shared in equal amounts by the particles and is irrespective of their temperatures  $\theta_i$  and  $\theta_j$ . On the other hand, we assume that the particles can also vary their internal energy by exchanging internal energy if  $\theta_i \neq \theta_j$ . The energy



transferred by this mechanism between the particles will be referred to as *mesoscopic heat flow*  $\dot{q}_{ij}^D$ . Associated with this dissipative current, a random heat flow  $\dot{q}_{ij}^R$  must also be added. Hence, we write

$$\dot{u}_i = -\frac{1}{2m}(\vec{p}_i - \vec{p}_j) \cdot (\vec{F}_{ij}^D + \vec{F}_{ij}^R) + \dot{q}_{ij}^D + \dot{q}_{ij}^R \quad (2.12)$$

with the requirement  $\dot{q}_{ij}^{D,R} = -\dot{q}_{ji}^{D,R}$  to ensure that eq. (2.11) is satisfied. Note that the r.h.s. of eq. (2.12) preserves Galilean-invariance.

So far, only the conservation equations have been used to find general properties to be satisfied by the dissipative forces and mesoscopic heat flows, referred to as *dissipative currents* in a wider sense from now on. In analogy with the Thermodynamics of Irreversible Processes[10], we can make use of the Gibbs equation, eq. (2.2) together with eq. (2.12) to find the *particle's entropy production* from the interaction between pairs, yielding

$$\dot{s}_i + \dot{s}_j = \frac{\dot{u}_i}{\theta_i} + \frac{\dot{u}_j}{\theta_j} = -\frac{1}{m} \left( \frac{1}{\theta_i} + \frac{1}{\theta_j} \right) (\vec{p}_i - \vec{p}_j) \cdot \vec{F}_{ij}^D + \left( \frac{1}{\theta_i} - \frac{1}{\theta_j} \right) \dot{q}_{ij}^D \geq 0 \quad (2.13)$$

where only the deterministic part of the interactions has explicitly been considered, according to point 5. The inequality in this last equation is the expression of the Second Law of Thermodynamics, indicating the irreversibility of the particle's dissipative interactions. From the entropy production equation the so-called *thermodynamic forces* can be identified as the factors multiplying the respective dissipative currents,  $\vec{F}_{ij}^D$  and  $\dot{q}_{ij}^D$  in eq. (2.13). Thus, in the spirit of the Thermodynamics of Irreversible Processes[10] we propose a linear relation between the dissipative currents and the thermodynamic forces of the form

$$\vec{F}_{ij}^D = L_{ij}^{(p)} \frac{1}{m} \left( \frac{1}{\theta_i} + \frac{1}{\theta_j} \right) \hat{r}_{ij} \hat{r}_{ij} \cdot (\vec{p}_j - \vec{p}_i) \quad (2.14)$$

$$\dot{q}_{ij} = L_{ij}^{(q)} \left( \frac{1}{\theta_i} - \frac{1}{\theta_j} \right) \quad (2.15)$$

The functions  $L_{ij}^{(p)}$  and  $L_{ij}^{(q)}$  are analogous to the so-called Onsager coefficients[10]. Due to the different tensorial natures of the momentum flux and the heat flux, these phenomena are not coupled in eqs. (2.14) and (2.15) (Curie's theorem[10]). The

mesoscopic Onsager coefficients introduced in eqs. (2.14) and (2.15) must satisfy the following conditions so that the system can reach the proper thermodynamic equilibrium

1. The thermodynamic forces are Galilean-invariant, as are the dissipative currents. This implies that the Onsager coefficients must also be Galilean-invariant.
2. Microscopic reversibility implies that  $L_{ij}^{(p)}$  and  $L_{ij}^{(q)}$  must be even functions under time-reversal[14].
3. Since the thermodynamic forces change their sign under the exchange  $i \rightarrow j$ , then  $L_{ij}^{(p)}$  and  $L_{ij}^{(q)}$  must be *invariant* under this transformation. This fact is crucial in the derivation of the transport properties of the system.

In the *linear* Non-Equilibrium Thermodynamics scheme,  $L_{ij}^{(p)}$  and  $L_{ij}^{(q)}$  are constants. However, this choice restricts the expression for the macroscopic transport coefficients of the model to a given particular form which, in addition, seldom occurs in nature[11]. Thus, we will consider a general dependence of the Onsager coefficients in both the distance  $r_{ij}$  and the temperatures of the particles  $\theta_i$  and  $\theta_j$ , in order to allow the model to describe the temperature dependence of the macroscopic transport coefficients. Thus, for convenience, let us rewrite eqs. (2.14) and (2.15) in a different form

$$\vec{F}_{ij}^D = \zeta_{ij} \frac{1}{m} \hat{r}_{ij} \hat{r}_{ij} \cdot (\vec{p}_j - \vec{p}_i) \quad (2.16)$$

$$\dot{q}_{ij} = \lambda_{ij} (\theta_j - \theta_i) \quad (2.17)$$

Written in this way, these expressions are reminiscent of the macroscopic phenomenological Newton's law for the transport of momentum, and Fourier's law for heat transport[10]. Hence,  $\zeta_{ij}$  is a mesoscopic analog of the macroscopic viscosity and  $\lambda_{ij}$ , of the thermal conductivity.  $\zeta_{ij}$  and  $\lambda_{ij}$  will be referred to as *mesoscopic* dissipative coefficients, from now on. Clearly, the mesoscopic dissipative coefficients are related to the mesoscopic Onsager coefficients introduced in eqs. (2.14) and

(2.15), according to

$$L_{ij}^{(p)} = \Theta_{ij} \zeta_{ij} \quad (2.18)$$

$$L_{ij}^{(q)} = \theta_i \theta_j \lambda_{ij} \quad (2.19)$$

where  $\Theta_{ij}^{-1} \equiv (1/\theta_i + 1/\theta_j)/2$ . In what follows, we will use the mesoscopic dissipative coefficients instead of the mesoscopic Onsager coefficients, to base our discussion in the most intuitive manner. From eqs. (2.18) and (2.19) one can see that if  $\zeta_{ij}$  and  $\lambda_{ij}$  are constants, then the mesoscopic Onsager coefficients depend on the particles' internal energy through the temperatures  $\theta_i$  and  $\theta_j$ . The presence of temperature-dependencies in the mesoscopic Onsager coefficients will introduce subtleties in the derivation of the algorithm due to the so-called Itô-Stratonovich dilemma[16] that we will discuss later on.

The properties of the random terms are also chosen to parallel the theory of hydrodynamic fluctuations[11, 12]. Since  $\vec{F}_{ij}^D$  and  $\dot{q}_{ij}^D$  are not coupled, we will demand that the random terms  $\vec{F}_{ij}^R$  and  $\dot{q}_{ij}^R$  be statistically independent. They can be written in the form

$$\vec{F}_{ij}^R = \hat{r}_{ij} \Gamma_{ij} \mathcal{F}_{ij}(t) \quad \text{and} \quad \dot{q}_{ij}^R = \text{Sign}(i - j) \Lambda_{ij} \mathcal{Q}_{ij}(t) \quad (2.20)$$

where the function  $\text{Sign}(i - j)$  is 1 if  $i > j$  and  $-1$  if  $i < j$ , ensuring that  $\dot{q}_{ji}^R = -\dot{q}_{ij}^R$ . The scalar random variables  $\mathcal{F}_{ij}$  and  $\mathcal{Q}_{ij}$  are stationary, Gaussian and white[14, 15], with zero mean and correlations

$$\langle \mathcal{F}_{ij}(t) \mathcal{F}_{kl}(t') \rangle = \langle \mathcal{Q}_{ij}(t) \mathcal{Q}_{kl}(t') \rangle = (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \delta(t - t') \quad (2.21)$$

$$\langle \mathcal{F}_{ij}(t) \mathcal{Q}_{kl}(t') \rangle = \langle \mathcal{Q}_{ij}(t) \mathcal{F}_{kl}(t') \rangle = 0 \quad (2.22)$$

$\Gamma_{ij}$  and  $\Lambda_{ij}$  are functions to be determined later. Note that  $\zeta_{ij}$  and  $\Gamma_{ij}$  are, respectively,  $\gamma\omega_D$  and  $\sigma\omega_R$  in ref.[5].

### 2.2.1 Derivation of the algorithm

As we have seen, the dynamics of the model is described by the set of Langevin equations, eqs. (2.6), (2.7) and (2.12), the definition of the dissipative currents,

eqs. (2.16) and (2.17), and the random forces, eqs. (2.20). To derive an algorithm describing such a stochastic process, let us integrate these Langevin equations for a small increment of time  $\delta t$  and retain terms up to  $\mathcal{O}(\delta t)$ . One obtains

$$\vec{r}'_i = \vec{r}_i + \frac{\vec{p}_i}{m} \delta t \quad (2.23)$$

$$\vec{p}'_i = \vec{p}_i + \left\{ \vec{F}_i^{ext} + \sum_{j \neq i} \left[ \vec{F}_{ij}^C + \frac{\zeta_{ij}}{m} (\vec{p}_j - \vec{p}_i) \cdot \hat{r}_{ij} \hat{r}_{ij} \right] \right\} \delta t + \sum_{j \neq i} \hat{r}_{ij} \Gamma'_{ij} \delta t^{1/2} \Omega_{ij}^{(p)} \quad (2.24)$$

$$u'_i = u_i + \sum_{j \neq i} \left\{ \frac{\zeta_{ij}}{2m^2} [(\vec{p}_j - \vec{p}_i) \cdot \hat{r}_{ij}]^2 + \lambda_{ij} (\theta_j - \theta_i) \right\} \delta t + \sum_{j \neq i} \left\{ \frac{1}{2m} (\vec{p}'_j - \vec{p}'_i) \cdot \hat{r}_{ij} \Gamma'_{ij} \delta t^{1/2} \Omega_{ij}^{(p)} + \text{Sign}(i - j) \Lambda'_{ij} \delta t^{1/2} \Omega_{ij}^{(q)} \right\} \quad (2.25)$$

where  $\vec{r}'_i \equiv \vec{r}_i(t + \delta t)$ ,  $\vec{p}'_i \equiv \vec{p}_i(t + \delta t)$ , and  $u'_i \equiv u_i(t + \delta t)$  while  $\vec{r}_i$ ,  $\vec{p}_i$  and  $u_i$  are the value of these functions at time  $t$ , and  $\Gamma'_{ij}$  and  $\Lambda'_{ij}$  stand for the value of these functions when their arguments are calculated at the time  $t + \delta t$ . The integrals over the random terms have been interpreted as [16]

$$\int_t^{t+\delta t} d\tau \hat{r}_{ij}(\tau) \Gamma_{ij}[\tau] \mathcal{F}_{ij}(\tau) = \hat{r}_{ij}(t) \Gamma_{ij}[t + \delta t] \delta t^{1/2} \Omega_{ij}^{(p)} \quad (2.26)$$

in eq. (2.24), and

$$\begin{aligned} & \int_t^{t+\delta t} d\tau (\vec{p}_j(\tau) - \vec{p}_i(\tau)) \cdot \hat{r}_{ij}(\tau) \Gamma_{ij}[\tau] \mathcal{F}_{ij}(\tau) \\ &= (\vec{p}_j(t + \delta t) - \vec{p}_i(t + \delta t)) \cdot \hat{r}_{ij}(t) \Gamma_{ij}[t + \delta t] \delta t^{1/2} \Omega_{ij}^{(p)} \end{aligned} \quad (2.27)$$

$$\int_t^{t+\delta t} d\tau \text{Sign}(i - j) \Lambda_{ij}[\tau] \mathcal{Q}_{ij}(\tau) = \text{Sign}(i - j) \Lambda_{ij}[t + \delta t] \delta t^{1/2} \Omega_{ij}^{(q)} \quad (2.28)$$

respectively, in eq. (2.25). In these equations, we have defined the random numbers

$$\Omega_{ij}^{(p)} \equiv \frac{1}{\delta t^{1/2}} \int_t^{t+\delta t} d\tau \mathcal{F}_{ij}(\tau) \quad \text{and} \quad \Omega_{ij}^{(q)} \equiv \frac{1}{\delta t^{1/2}} \int_t^{t+\delta t} d\tau \mathcal{Q}_{ij}(\tau) \quad (2.29)$$

which are Gaussian, with zero mean and correlations  $\langle \Omega_{ij}^{(p)} \Omega_{kl}^{(p)} \rangle = \langle \Omega_{ij}^{(q)} \Omega_{kl}^{(q)} \rangle = (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk})$  and  $\langle \Omega_{ij}^{(p)} \Omega_{kl}^{(q)} \rangle = 0$ , according to eqs. (2.21) and (2.22). Eqs. (2.26), (2.27) and (2.28) express the fact that the amplitudes of the random forces may depend on the fast variables themselves ( $u_i$  through the temperature  $\theta_i$ , in this case), introducing the so-called Itô-Stratonovich dilemma [16]. Here, we have chosen an interpretation rule that is neither that of Itô nor Stratonovich, but has the

property that the resulting stochastic process, once the amplitudes of the random terms have been fixed, satisfies detailed balance up to  $\mathcal{O}(\delta t)$ [27]. Note that in eqs. (2.26), (2.27) and (2.28) the slow variable  $\vec{r}_{ij}$  is taken at  $t$  instead of at  $t + \delta t$ , since the difference between both considerations is of order  $\mathcal{O}(\delta t^{3/2})$ ; only fast variables, whose increments contain terms of the order  $\mathcal{O}(\delta t^{1/2})$ , need to be taken at the latest time since they introduce terms of order  $\mathcal{O}(\delta t)$  in the algorithm. That the stochastic process introduced by eqs.(2.23), (2.24), and (2.25) satisfies detailed balance can be verified from the functional form of the resulting Fokker-Planck equation, since this is a property of the transition probabilities and the equilibrium distribution[16]. Other algorithms have been proposed that explicitly incorporate time-reversibility in the equations of motion for the particles [24], which eventually leads to the resulting stochastic process satisfying detailed balance[25]. The forward interpretation rule, however, permits us to straightforwardly relate the differential equations for the change in the particle's variables (Langevin equations) with an Euler algorithm that will lead to the *proper thermodynamic equilibrium* for the system.

To obtain a causal or explicit form of the algorithm defined in eqs. (2.23), (2.24) and (2.25), we expand the right hand side of these equations in powers of  $\delta t$  and retain terms of up to first order. We then obtain

$$\delta \vec{r}_i = \frac{\vec{p}_i}{m} \delta t \quad (2.30)$$

$$\begin{aligned} \delta \vec{p}_i = & \left\{ \vec{F}_i^{ext} + \sum_{j \neq i} \left[ \vec{F}_{ij}^C + \left( \frac{\zeta_{ij}}{m} + \frac{1}{2m} \Gamma_{ij} \left( \frac{\partial}{\partial u_i} + \frac{\partial}{\partial u_j} \right) \Gamma_{ij} \Omega_{ij}^{(p)^2} \right) (\vec{p}_j - \vec{p}_i) \cdot \hat{r}_{ij} \hat{r}_{ij} \right. \right. \\ & \left. \left. + \hat{r}_{ij} \text{Sign}(i - j) \Lambda_{ij} \left( \frac{\partial}{\partial u_i} - \frac{\partial}{\partial u_j} \right) \Gamma_{ij} \Omega_{ij}^{(p)} \Omega_{ij}^{(q)} \right] \right\} \delta t + \sum_{j \neq i} \hat{r}_{ij} \Gamma_{ij} \delta t^{1/2} \Omega_{ij}^{(p)} \end{aligned} \quad (2.31)$$

$$\begin{aligned} \delta u_i = & \sum_{j \neq i} \left\{ \frac{1}{2m} \left( \frac{\zeta_{ij}}{m} + \frac{1}{2m} \Gamma_{ij} \left( \frac{\partial}{\partial u_i} + \frac{\partial}{\partial u_j} \right) \Gamma_{ij} \Omega_{ij}^{(p)^2} \right) ((\vec{p}_j - \vec{p}_i) \cdot \hat{r}_{ij})^2 + \lambda_{ij} (\theta_j - \theta_i) \right. \\ & + \frac{1}{2m} (\vec{p}_j - \vec{p}_i) \cdot \hat{r}_{ij} \Omega_{ij}^{(p)} \Omega_{ij}^{(q)} \text{Sign}(i - j) \left[ \Gamma_{ij} \left( \frac{\partial}{\partial u_i} + \frac{\partial}{\partial u_j} \right) \Lambda_{ij} - \Lambda_{ij} \left( \frac{\partial}{\partial u_j} - \frac{\partial}{\partial u_i} \right) \Gamma_{ij} \right] \\ & - \Lambda_{ij} \left( \frac{\partial}{\partial u_j} - \frac{\partial}{\partial u_i} \right) \Lambda_{ij} \Omega_{ij}^{(q)^2} - \frac{1}{m} \Gamma_{ij}^2 \Omega_{ij}^{(p)^2} \left. \right\} \delta t \\ & + \sum_{j \neq i} \left\{ \frac{1}{2m} (\vec{p}_j - \vec{p}_i) \cdot \hat{r}_{ij} \Gamma_{ij} \delta t^{1/2} \Omega_{ij}^{(p)} + \Lambda_{ij} \delta t^{1/2} \Omega_{ij}^{(q)} \right\} \end{aligned} \quad (2.32)$$

Eqs. (2.30), (2.31) and (2.32) is an explicit algorithm, equivalent to the implicit algorithm given in eqs. (2.23), (2.24) and (2.25) up to order  $\mathcal{O}(\delta t)$ . By using standard methods[16], from eqs. (2.30), (2.31) and (2.32) one obtains the Fokker-Planck equation

$$\frac{\partial}{\partial t} P(\{\vec{r}_i\}, \{\vec{p}_i\}, \{u_i\}) = L^{con} P(\{\vec{r}_i\}, \{\vec{p}_i\}, \{u_i\}) + L^{dif} P(\{\vec{r}_i\}, \{\vec{p}_i\}, \{u_i\}) \quad (2.33)$$

where the *convective* operator,  $L^{con}$ , and the *diffusive* operator,  $L^{dif}$ , are defined as

$$\begin{aligned} L^{con} \equiv & -\sum_{i=1}^N \left[ \frac{\partial}{\partial \vec{r}_i} \cdot \frac{\vec{p}_i}{m} + \frac{\partial}{\partial \vec{p}_i} \cdot \vec{F}_i^{ext} \right] - \sum_{i,j \neq i}^N \left\{ \frac{\partial}{\partial \vec{p}_i} \cdot \left[ \vec{F}_{ij}^C + \frac{\zeta_{ij}}{m} \hat{r}_{ij} \hat{r}_{ij} \cdot (\vec{p}_j - \vec{p}_i) \right] + \right. \\ & \left. + \frac{\partial}{\partial u_i} \left[ \frac{\zeta_{ij}}{2m^2} [(\vec{p}_j - \vec{p}_i) \cdot \hat{r}_{ij}]^2 + \lambda_{ij} (\theta_j - \theta_i) \right] \right\} \end{aligned} \quad (2.34)$$

$$\begin{aligned} L^{dif} \equiv & \sum_{i,j \neq i}^N \left\{ \frac{\partial}{\partial \vec{p}_i} \cdot \frac{1}{2} \Gamma_{ij}^2 \hat{r}_{ij} \hat{r}_{ij} \cdot \vec{\mathcal{L}}_{ij} + \frac{\partial}{\partial u_i} \left[ \frac{1}{2m} (\vec{p}_j - \vec{p}_i) \cdot \frac{1}{2} \Gamma_{ij}^2 \hat{r}_{ij} \hat{r}_{ij} \cdot \vec{\mathcal{L}}_{ij} + \frac{1}{2} \Lambda_{ij}^2 \left( \frac{\partial}{\partial u_i} - \frac{\partial}{\partial u_j} \right) \right] \right\} \end{aligned} \quad (2.35)$$

where we have in addition defined the operator

$$\vec{\mathcal{L}}_{ij} \equiv \left( \frac{\partial}{\partial \vec{p}_i} - \frac{\partial}{\partial \vec{p}_j} \right) + \frac{1}{2m} (\vec{p}_j - \vec{p}_i) \left( \frac{\partial}{\partial u_i} + \frac{\partial}{\partial u_j} \right) \quad (2.36)$$

Note that the algorithm giving the aforementioned Fokker-Planck equation is not unique. Effectively, the terms of order  $\mathcal{O}(\delta t)$  in eqs. (2.30), (2.31) and (2.32) can be replaced by their averages over the random terms, giving a much simpler algorithm satisfying the same Fokker-Planck equation, eq. (2.33). Such a procedure was adopted in the first version of the DPDE model[18]. However, replacing the drift terms by their averages means that the energy is only conserved *in the mean* but not at *every time-step*. The implicit algorithm shown in eqs. (2.23), (2.24) and (2.25) is thus a more compact form satisfying the desired properties of the DPDE model described.

The amplitudes of the random terms are derived by imposing that the equilibrium distribution function given in eq. (2.4) is a stationary solution of eq. (2.33), thus yielding the fluctuation-dissipation theorems

$$\Gamma_{ij}^2 = 2k L_{ij}^{(p)} = 2k \zeta_{ij} \Theta_{ij} \quad (2.37)$$

$$\Lambda_{ij}^2 = 2k L_{ij}^{(q)} = 2k \theta_i \theta_j \lambda_{ij} \quad (2.38)$$

Eq. (2.33), in view of the definitions (2.34), (2.35) and (2.36), together with the expressions for the amplitudes of the random terms (2.37) and (2.38), satisfies the expected detailed balance condition[14].

The fluctuation-dissipation theorems given in eqs. (2.37) and (2.38) are the generalization of the results previously obtained in ref.[18], to the case of an arbitrary temperature-dependence of the mesoscopic coefficients. We have to stress the fact that the amplitude of the random force  $\Gamma_{ij}$  depends only on particle variables and that it is *independent of the macroscopic state* of the system (the thermodynamic temperature, for instance). This point is a crucial difference between the DPDE model and the previous isothermal DPD models, with no energy conservation. For the isothermal DPD model, the amplitude of the random force is proportional to the thermodynamic temperature of the system  $T$  which must be previously specified. This particular feature of the actual DPDE allows one to model temperature gradients in the systems as well as heat flows. Furthermore, since the dynamics is based on particle properties, DPDE can deal with systems either in contact with a heat reservoir or with isolated systems.

Having set the fluctuation-dissipation theorems that fix the amplitude of the random terms, the algorithm describing the DPDE process is completely specified.

### 3 Thermodynamics of the DPDE model

The properties of the DPDE system defined so far are such that the system evolves irreversibly towards a final equilibrium state. If the system is in contact with a heat reservoir, such an equilibrium state is characterized by the probability distribution given in eq. (2.4). Since this fact allows us to define a thermodynamics for the system of dissipative particles, we will devote this section to the calculation of general results valid for any model.

Let us introduce a partition function in a classical sense,  $Q(T, V, N)$ , as

$$\begin{aligned} Q(T, V, N) &\equiv \frac{1}{N!h^{3N}} \int \left( \prod_i d\vec{p}_i d\vec{r}_i du_i \right) e^{-H(\{\vec{r}_i\}, \{\vec{p}_i\})/kT} \prod_i e^{s_i(u_i)/k - u_i/kT} \\ &\equiv Q_H(T, V, N) Q_{int}(T, N) \end{aligned} \quad (3.1)$$

where  $Q_H$  refers to the partition function of the "hamiltonian" part of the interaction and  $Q_{int}$ , to the partition function of the internal degrees of freedom. The factor  $1/h^{3N}$  has been introduced in analogy with the partition function of a physical system. The equivalent Free Energy for the system of dissipative particles can thus be obtained as a sum of two contributions

$$\mathcal{F}(T, V, N) = -kT \ln Q_H(T, V, N) - kT \ln Q_{int}(T, N) \quad (3.2)$$

The former is related to the hamiltonian part of the dynamics and the latter, related to the internal energy dynamics.  $Q_H$ , can be obtained from the Hamiltonian of the system given in eq. (2.1). One gets

$$\begin{aligned} Q_H(T, V, N) &= \frac{1}{N!h^{3N}} \int \left( \prod_i d\vec{p}_i d\vec{r}_i \right) e^{-H(\{\vec{r}_i\}, \{\vec{p}_i\})/kT} \\ &= \frac{1}{\Lambda^{3N} N!} \int \prod_i d\vec{r}_i e^{-\sum_i [\psi^{ext}(\vec{r}_i) + \sum_{j>i} \psi(r_{ij})]/kT} \equiv \frac{1}{\Lambda^{3N} N!} Z_H(T, V, N) \end{aligned} \quad (3.3)$$

where  $\Lambda \equiv h/\sqrt{2\pi mkT}$  is the de Broglie wavelength and  $Z_H(T, V, N)$  is the so-called *configurational integral*[17]. The internal partition function can also be worked out. Effectively, one has

$$Q_{int}(T, N) = \int \prod_i du_i \prod_i e^{s_i(u_i)/k - u_i/kT} = \left[ \int du e^{s(u)/k - u/kT} \right]^N \equiv [Q_1(T)]^N \quad (3.4)$$

hence factorizing in one-particle partition functions, depending only on the temperature.

Using these expressions, the free energy takes the form

$$F(T, V, N) = kTN(\ln \rho + 3 \ln \Lambda - 1) - kT \ln \frac{Z_H(T, V, N)}{V^N} - kTN \ln Q_1(T) \quad (3.5)$$

Note that  $Q_{int}$  is a function of the temperature and the number of particles, but is independent of the volume. Therefore, the pressure of the system is completely



determined by the Hamiltonian interactions between particles, as one could have intuitively guessed. The internal energy, however, contains contributions from all the terms.

The explicit knowledge of the *equations of state* of the system of DPD particles are very useful, since they can be used to compare with the equations of state of a real system when simulating its behaviour and properties in a computer. In the rest of this section we will derive general equations of state for the pressure and also for the internal energy of the system, in terms of microscopic parameters of the model. The analysis given here will follow that of ref.[17], where the details of the calculation can be found. Let us introduce the one-particle and the two-particle distribution functions, according to the relationships

$$\rho(\vec{r}) \equiv \left\langle \sum_i \delta(\vec{r} - \vec{r}_i) \right\rangle, \quad (3.6)$$

for the former, and

$$\rho^{(2)}(\vec{r}, \vec{r}') \equiv \left\langle \sum_{i,j \neq i} \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_j) \right\rangle \quad (3.7)$$

for the latter. The averages refer to the equilibrium probability distribution for the DPD system given in eq. (2.4). For a homogeneous and isotropic system, these expressions can be further simplified. Effectively, the one-particle distribution function is the mean density  $\rho(\vec{r}) = N/V$  and the two-particle distribution function reduces to

$$\rho^{(2)}(|\vec{r} - \vec{r}'|) = \rho^2 g(|\vec{r} - \vec{r}'|) \quad (3.8)$$

where this last equation is in fact a definition of the pair-distribution function  $g(r)$ .

The pressure equation can be obtained from the so-called *virial equation*

$$\frac{\beta P}{\rho} = 1 + \frac{\beta}{3N} \left\langle \sum_i \vec{r}_i \cdot \frac{\partial}{\partial \vec{r}_i} \sum_{j,k > j} \psi(r_{jk}) \right\rangle \quad (3.9)$$

where  $\beta \equiv 1/kT$ . After some algebra, one arrives at the final expression[17]

$$\frac{\beta P}{\rho} = 1 - \frac{2\pi\beta\rho}{3} \int_0^\infty dr r^3 \frac{\partial\psi(r)}{\partial r} g(r) \quad (3.10)$$

From this expression one can see that the actual model of DPDE particles can exhibit the same phase behaviour as a fluid of pair interaction potentials, thus *gas*, *liquid* and *solid* phases can be modelled. The actual DPDE shares this property with the older versions of the DPD model.

The internal energy of the system can be obtained by performing the equilibrium average of all the contributions to this quantity

$$U = \int d\vec{r} \left\langle \sum_i \frac{p_i^2}{2m} \delta(\vec{r} - \vec{r}_i) \right\rangle + \int d\vec{r} d\vec{r}' \left\langle \sum_{i,j>i} \psi(r_{ij}) \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_j) \right\rangle + \int d\vec{r} \left\langle \sum_i u_i \delta(\vec{r} - \vec{r}_i) \right\rangle \quad (3.11)$$

Again, after some algebra, we obtain

$$U = \frac{3}{2} N k T + N \Psi + N e_u \quad (3.12)$$

where the first term on the right hand side of this equation is the ideal gas contribution. The second term is the interaction potential energy contribution, and is given by

$$\Psi \equiv 2\pi \frac{N}{V} \int dr r^2 g(r) \psi(r) \quad (3.13)$$

The third term is the contribution due to the internal energy of the particles to the macroscopic internal energy of the system. It is evaluated from the integral

$$e_u = \frac{\int_0^\infty du u e^{s(u)/k - u/kT}}{\int_0^\infty du e^{s(u)/k - u/kT}} \quad (3.14)$$

Note that the thermal capacity of the system is obtained by differentiation,  $\partial U / \partial T)_v$ . This can be used to relate the function  $s(u)$ , that has to be supplied to the model, with the thermal behaviour of a given real system. These expressions cannot be further developed without explicit calculation of the pair distribution function. However, they can shed some light on the relevant aspects of the thermodynamic equilibrium in the DPDE system.

To end this section, let us introduce a non-equilibrium extension of the free energy, given by the expression

$$\mathcal{F}[P] \equiv \int dX P(X, t) \{f(X) + kT \ln P(X, t)\} \quad (3.15)$$

which is defined as a functional of the actual probability distribution  $P$ , and where  $X$  is a point in phase space,  $(\{\vec{p}_i\}, \{\vec{r}_i\}, \{u_i\})$ , and the function  $f(X)$  is defined as

$$f(X) = H(\{\vec{p}_i\}, \{\vec{r}_i\}) + \sum_i (u_i - T s_i(u_i)) = -kT \ln P_e(X) \quad (3.16)$$

Using this expression for the function  $f(X)$ , the eq. (3.15) can be cast in a more convenient form

$$\mathcal{F}[P] = \int dX kT P(X, t) \ln \frac{P(X, t)}{P_e(X)} \quad (3.17)$$

This functional  $\mathcal{F}$  satisfies an  $H$ -theorem,  $\partial \mathcal{F} / \partial t \leq 0$ , as follows from differentiation of eq. (3.17) with respect to time, with the use of the Fokker-Planck equation given in eq. (2.33) together with the fluctuation-dissipation theorems (2.37) and (2.38).

### 3.1 Analysis of a particular system

In the remainder of this section we will analyze a particular model and show some simulation results.

Let us consider the case in which the DPDE particles have no interaction potential forces. The definition of the model requires a *particle equation of state* relating the particle's entropy with the particle's internal energy,  $s(u_i)$ . The simplest model is to assume that the particle temperature is a linear function of the particle internal energy of the form  $u_i = \phi \theta_i$ , where  $\phi$  is a constant playing the role of a particle's heat capacity. We will take  $\phi$  to be larger than the Boltzmann constant  $k$ [23]. Hence, the particle internal energy probability distribution takes the form

$$P_e(u_i) \sim e^{s(u_i)/k - u_i/kT} = u^{\phi/k} e^{-u_i/kT} \quad (3.18)$$

In the absence of an interparticle interaction potential the position probability distribution is uniform, and the momentum distribution is that of Maxwell-Boltzmann

$$P_e(\vec{p}_i) \sim e^{-\frac{p_i^2}{2mkT}} \quad (3.19)$$

The model is then analogous to a general ideal gas and, hence, it corresponds to a single gas phase, as seen from the resulting pressure equation

$$p = kT \rho, \quad (3.20)$$

in view of eq. (3.10). The second equation of state determining the thermodynamic state of the system, follows from eq. (3.12) and gives the variation of the macroscopic internal energy with respect to the state variables. For our particular model, one gets

$$U = \frac{3}{2}NkT + NkT \left( \frac{\phi}{k} + 1 \right) \quad (3.21)$$

In this equation, the first term is the ideal gas contribution to the macroscopic internal energy, due to the translational degrees of freedom of the particles. The second term,  $\phi T$ , is the internal energy stored per particle. Note, however, the additional  $kT$  on the right hand side of eq. (3.21), that comes from the extra degree of freedom due to the fluctuations in the internal energy of the particles. The heat capacity can be calculated by differentiating eq. (3.21) with respect to the temperature, giving

$$C_v = Nk \left( \frac{\phi}{k} + \frac{5}{2} \right) \quad (3.22)$$

Let us point out that eq. (3.22) is a relationship between macroscopically measurable magnitudes of any real system,  $C_v$ , with model parameters  $\phi$ .

As far as the dynamic properties are concerned, the particle friction and thermal conductivity are given by the expressions

$$\zeta_{ij} = \zeta_0 \left( 1 - \frac{r_{ij}}{r_\zeta} \right)^2 \quad \text{for } r_{ij} \leq r_\zeta \quad (3.23)$$

$$\lambda_{ij} = \frac{L_0^{(q)}}{\theta_i \theta_j} \left( 1 - \frac{r_{ij}}{r_\lambda} \right)^2 \quad \text{for } r_{ij} \leq r_\lambda \quad (3.24)$$

where  $\zeta_0$  and  $L_0^{(q)}$  are constants giving the magnitude of the mesoscopic friction and thermal conductivity, respectively, and  $r_\zeta$  and  $r_\lambda$  are the respective ranges of the dissipative interactions. The functions  $\zeta_{ij}$  and  $\lambda_{ij}$  vanish if  $r_{ij} > r_\zeta$  and  $r_{ij} > r_\lambda$ , respectively. Although other choices could be made for the spatial dependence of  $\zeta_{ij}$  and  $\lambda_{ij}$ , we have made here the usual choice[1].

The explicit derivation of the *macroscopic* transport properties of the system will be treated elsewhere. Here, however, we give results that can be easily calculated by considering that the transport of momenta and energy is dominated by the dissipative interactions. Such a limit must be reached under conditions of high density

system or by choosing large particle friction and thermal conductivity parameters. By considering the particles as frozen and analyzing the transport of mesoscopic heat through a hypothetical plane dividing the system into two parts[26], one obtains for the macroscopic thermal conductivity in these limiting conditions

$$\tilde{\lambda} \simeq \frac{\rho^2}{T^2} \frac{2\pi}{3} \int_0^{r_\lambda} dr r^4 L_0^{(q)} \left(1 - \frac{r_{ij}}{r_\lambda}\right)^2 g(r) \quad (3.25)$$

A similar calculation for the transport of momentum yields the shear viscosity

$$\eta \simeq \frac{2\pi\rho^2}{15} \int_0^{r_\zeta} dr r^4 \zeta_0 \left(1 - \frac{r_{ij}}{r_\zeta}\right)^2 g(r) \quad (3.26)$$

which coincides with the result obtained in ref.[6] when the particle friction coefficient is considered as very large. Performing the integrals given in eqs. (3.25) and (3.26) by using the fact that in equilibrium and in the absence of pair interaction potentials,  $g(r) = 1$ , we then obtain for the viscosity

$$\eta = \frac{2\pi\rho^2}{1575} r_\zeta^5 \zeta_0 \quad (3.27)$$

For the macroscopic thermal conductivity, one gets

$$\tilde{\lambda} = \frac{2\pi}{315} \frac{\rho^2}{T^2} L_0^{(q)} r_\lambda^5 \quad (3.28)$$

The analysis of the simulation results with steady state heat conduction shows agreement with the functional dependence given in eq. (3.28). A future publication will be devoted to a deeper analysis of the transport properties of the DPDE model.

The velocity of sound is theoretically obtained by means of a thermodynamic calculation

$$c^2 = \left( \frac{\partial P}{\partial \rho} \right)_S = \left( \frac{C_p}{C_v} \frac{\partial P}{\partial \rho} \right)_T \quad (3.29)$$

For the case under discussion, one obtains for the speed of sound the ideal gas result

$$c^2 = \frac{\phi + 7k/2}{\phi + 5k/2} \frac{kT}{m} \quad (3.30)$$

In order to carry out the simulations, we have introduced dimensionless variables suitable for a proper interpretation of the results. We have defined a temperature

of reference  $T_R$  to be used as the scale of temperature. Thus,  $T = T_R T^*$  and  $\theta_i = T_R \theta_i^*$ , where the asterisk is used to denote a dimensionless variable from now on. The momentum of the particles is made dimensionless according with  $\vec{p}_i = \vec{p}_i^* \sqrt{2mkT_R}$ , using the characteristic value of the momentum in a system with no externally imposed flow and thermal fluctuations:  $\sqrt{\langle p_i^2 \rangle}$ . The penetration depth for the momentum defines a characteristic length scale  $l = \sqrt{2mkT_R}/\zeta_0$ . Thus,  $\vec{r}_i = \vec{r}_i^* l$ . The characteristic scale of time is the relaxation time for the particle's momentum, that is  $t = t^* m/\zeta_0$ . The characteristic scale for the particle's internal energy is chosen to be  $\phi T_R$  so that  $u_i = u_i^* \phi T_R$ . When the algorithm is written in terms of these dimensionless variables it can be seen that there are only two independent dimensionless parameters in the model described in this section, that is

$$B \equiv \frac{k}{\phi} \quad (3.31)$$

$$C \equiv \frac{m L_0^{(q)}}{\zeta_0 \phi T_R^2} \quad (3.32)$$

$B$  measures the relative magnitude of the fluctuations in the particle's internal energy with the characteristic particle energy. It is thus convenient that  $B$  be small.  $C$  is the ratio between a relaxation time for momentum decay  $m/\zeta_0$ , and the relaxation time for the decay of a particle's internal energy fluctuations  $\phi T_R^2/L_0^{(q)}$ . Note that, to avoid negative values of the particle's internal energy during the integration of the algorithm (eqs. (2.23), (2.24 and (2.25)), in the presence of externally imposed temperature gradients, one can roughly estimate that

$$C \left( \frac{4\pi}{3} r_\lambda^{*3} \right) \rho^* (r_\lambda^* \nabla^* T^*) \delta t^* \ll 1 \quad (3.33)$$

where  $\rho^*$  is the dimensionless particle number density and  $\delta t^*$  is the dimensionless integration time step. The fluctuating part of the energy can also lead to negative energy values if the condition

$$\sqrt{BC} \delta t^* \left( \frac{4\pi}{3} r_\lambda^{*3} \right) \rho^* \ll 1 \quad (3.34)$$

is not satisfied.

Two aspects of the DPDE model have been investigated using simulations in three dimensions. In the first place, the thermodynamic consistency has been

checked by measuring the equilibrium distributions for a system in contact with a heat reservoir. Figs. 1 and 2 show the momentum and particle's internal energy distributions of a system of  $N = 30000$  particles in contact with two walls at a temperature  $T^* = 1.1$ , while periodic boundary conditions are chosen for the other two dimensions in space. The factor  $B$  has been set equal to 0.01,  $C = 17$  and the cutoff lengths  $r_\lambda^*$  and  $r_\zeta^*$  are both set equal to 1.24. The size of the system is chosen such that  $\rho^* = 1$ , so that the dimensionless lateral size of the box is  $L^* = N^{1/3}$ . The number of particles interacting simultaneously with a given particle is thus determined by the size of  $r_\lambda^*$  and  $r_\zeta^*$ . For our values, we can roughly estimate that 8 particles interact at one time with a given particle.

The simulation has been initialised by a random distribution of particles at rest and a dimensionless particle temperature  $\theta_i^* = 1$ . At the initial stages of the simulation, the system is cooled down to a temperature of about 0.98 by the transformation of internal energy into kinetic energy due to the action of the random forces, in a time scale  $t^*$  of about 1. The difference in temperature between the wall and the bulk provokes a heat flow from the walls to the particles (see Fig 3). This process takes place in a much longer time scale, found of the order of 100, although this is clearly related to the overall size of the system. In Fig. 3 we show the time evolution of the mean temperature of the particles. After equilibration, this mean temperature reaches the same temperature as that of the walls. In addition, the three translational degrees of freedom are found to satisfy the probability distribution given in eq. (3.18) which, expressed in dimensionless form reads

$$P_e(p_{i,\alpha}^*) = \frac{1}{\sqrt{\pi T^*}} e^{-p_{i,\alpha}^{*2}/T^*} \quad (3.35)$$

where  $p_{i,\alpha}^*$  stands for any of the three components,  $\alpha$ , of the momentum of the  $i^{th}$  particle, and  $T^*$  is equal to the temperature of the wall, 1.1. In Fig.1, simulation and theoretical results are shown together. We find excellent agreement between simulated and theoretical distributions which, in addition, are rather insensitive to the time step, provided it is small ( $\delta t^* = 0.01$  in this simulation). In equilibrium, the average internal energy of the system is found to be  $U^* = 33828 \pm 1$ . The same

property calculated by eq.(3.21) (written in dimensionless form) yields the value  $U^* = 33825$ , showing excellent agreement with the simulation value.

The degree of freedom represented by the particle's internal energy also satisfies the probability distribution given in eq. (3.19). This distribution can also be cast in dimensionless form, yielding

$$P_e(u_i^*) = \frac{u_i^{*1/B} e^{-u_i^*/BT^*}}{(BT^*)^{\frac{B}{B+1}} \Gamma\left(\frac{B}{B+1}\right)} \quad (3.36)$$

where here  $\Gamma$  stands for the Euler Gamma function, and  $T^*$  is the temperature of the walls. Fig. 2, shows the theoretical predictions and simulation results for this probability distribution. Once more, the agreement is excellent. This result is non trivial in view of the fact that the functional form of the probability distribution for the energy is arbitrary, and depends on the choice made for the particle equation of state,  $u_i = \phi\theta_i$  in our case. We have found, however, that this probability distribution is much more sensitive to the time-step ( $\delta t^* = 0.0001$  in the simulation shown in Fig. 2). For a time step  $\delta t^* = 0.01$ , the deviations are less than 1%.

Finally, the pressure in the simulation can be obtained from the average force that the particles exert on the walls. For the previously mentioned system we have obtained the pressure from the simulation and found a value of  $P^* = 1.137 \pm 0.005$ . The theoretical value given from the equation of state eq. (3.20) is  $P^* = 1.1$ . Again we find a good agreement between simulation and theory.

Simulations of closed systems (with periodic boundary conditions in the three dimensions) have also been performed (this is possible because the algorithm depends on particle properties only). The DPDE system tends in this case towards a final thermodynamic equilibrium satisfying the aforementioned probability distributions for the one-particle variables. In this case, however, the probability distribution of the complete system is not separable as it was in the previous case. The final temperature attained for the system is in excellent agreement with that predicted from eq. (3.21), provided that the total energy of the system is known.

The second aspect analysed is the ability of the model to represent non-equilibrium



features of fluids under temperature gradients, an unattainable problem for the older DPD algorithms. We have performed simulations of a DPDE system with  $N = 100000$  particles in a cubic box of lateral size  $N^{1/3}$ , with four walls and periodic boundary conditions in the remaining direction. The walls were considered to be a two-dimensional surface which exert a repulsive force in the orthogonal direction on the particles. The range of this force is of the order of the range of the particle-particle interaction. As far as the wall-particle dissipative interactions are concerned, we have considered as being analogous to the particle-particle interactions. Hence when a particle is within the interaction range of a wall, it exchanges heat and exerts a force orthogonal to the wall as if the latter were a particle of infinite mass and heat capacity. Therefore, the walls act as heat reservoirs at a given specified temperature, and non-stick boundary conditions apply.

In the simulations, the two walls in the  $x$ -axis were kept at fixed temperatures of  $T_h^* = 2.8$  and  $T_c^* = 0.8$ , while the other two walls were adiabatic and were placed in the  $z$ -axis, along which a gravity field was imposed on the particles. Qualitatively, the gravity was weak enough not to cause an excessive density gradient along the  $z$ -axis, and the particle's thermal conductivity was chosen to be very small to emphasize the convective effects. Initially at rest, the system spontaneously evolved towards a stationary convection roll as seen in Fig. 4, where the arrows stand for the fluid velocity field. The velocity field has been calculated by dividing the space into boxes and averaging the velocity of the particles inside the box at a given instance of time. The fields obtained in this way show a rather marked variability due to the inherent stochastic nature of the algorithm and the limited number of particles inside a given box at a given time. The results shown in Fig. 4 are thus the result of averaging in time as well as in the  $y$ -direction, to have better statistics. In addition, the temperature profile has been obtained. We see in Fig. 5 that a non-linear temperature profile, due to the compressibility of the model, exists and is slightly tilted due to the convective flow. These results are in qualitative agreement with convective rolls observed in boxes and in numerical solutions of the Navier-Stokes equations for incompressible systems under the conditions described here.

The estimated Rayleigh number is of the order of 1000, by comparison with the numerical solution of the Navier-Stokes equations. In Fig. 6 we show the density profile given by the model, in which one can appreciate the combined effects of the temperature gradient and gravity field, merging into a diagonal density gradient, due to the compressibility of the system. It is interesting to note how this density profile affects the convection pattern in the system (Fig. 4), causing a displacement of the vortex centre towards the denser region, and also inducing a faster motion in the upper layers, as compared with the bottom of the box.

## 4 Conclusions

Various aspects of the *Dissipative Particle Dynamics with Energy Conservation* algorithm, already introduced in ref.[18], have been treated here in depth. In particular, emphasis has been placed on two major points. Firstly, the original DPDE algorithm has been extended in two ways: to incorporate arbitrary temperature-dependencies in the transport coefficients, and to assure that the algorithm conserves the energy at every time-step rather than in the mean, as in our previous algorithm[18]. Secondly, in this paper we have studied the thermodynamic properties modelled by the DPDE algorithm such as the free energy and equations of state, and shown agreement between the simulated and theoretically predicted probability distributions. To demonstrate the ability of the DPDE algorithm in simulating the hydrodynamic behaviour of fluids under non-equilibrium conditions, simulations have been carried out for a system with a temperature gradient orthogonal to a gravity field. The results show the expected convective pattern for the velocity field, as well as the corresponding tilted temperature profile. These points stress the inherent features of the new DPDE algorithm as compared with the isothermal versions.

With respect to the first major point, and with a view to the use of the DPD methodology for the simulation of the dynamics of real fluids, it was necessary to incorporate arbitrary dependencies of the transport coefficients in the temperature.

We have constructed an algorithm where the mesoscopic friction and heat conduction coefficients,  $\zeta_{ij}$  and  $\lambda_{ij}$ , respectively, can depend on the particle's temperature. One can compare eq. (3.23) with eq. (3.26), to see that both coefficients are independent of the temperature, neither the particle's nor the thermodynamic temperatures. Contrarily, the functional form of eq. (3.24) gives rise to the  $1/T^2$  dependence of the thermal conductivity coefficient. Of course, since eqs. (3.25) and (3.26) are approximate, there must exist additional temperature dependencies that may be due either to  $g(r)$  or to the kinetic transport of momentum and energy. Note that, the latter has been neglected in our derivation of the transport coefficients.

Another aspect worth mentioning in this context is our derivation of an implicit algorithm. This derivation has two important properties. On the one hand, the algorithm can be directly obtained from the Langevin equations used to formulate the problem of the DPD particle dynamics. We have simply introduced an interpretation rule of the random terms, when integrating the equations of motion in a  $\delta t$ , which is different from the usual Itô-Stratonovich interpretations. On the other hand, the resulting algorithm, with the proper fluctuation-dissipation theorems, straightforwardly satisfies detailed balance which is required for the model to behave in a thermodynamically consistent manner. Furthermore, since this algorithm has been directly obtained from the Langevin equations (2.6), (2.7), and (2.12), it satisfies energy conservation at every time step, as do the Langevin equations themselves.

We have also indicated that a family of different algorithms can lead to the same Fokker-Planck equation. Since the process is Gaussian, it is completely determined by the first and second moments of the probability distributions for the random variables. Thus, the defining trends of this family of algorithms is that these first and second moments be the same for all of them, up to the order of validity of the algorithm itself,  $\mathcal{O}(\delta t)$ . As an example, let us average eq. (2.31) with respect to the random number  $\Omega_{ij}^{(p)}$ , giving

$$\langle \delta \vec{p}_i \rangle = \vec{F}_i^{ext} + \sum_{j \neq i} \left[ \vec{F}_{ij}^C + \left( \frac{\zeta_{ij}}{m} + \frac{1}{2m} \Gamma_{ij} \left( \frac{\partial}{\partial u_i} + \frac{\partial}{\partial u_j} \right) \Gamma_{ij} \right) (\vec{p}_j - \vec{p}_i) \cdot \hat{r}_{ij} \hat{r}_{ij} \right] \quad (4.1)$$

The same result is obtained from our previous algorithm proposed in eq. (16) of

ref.[18]. This demonstrates that indeed the firsts moments of the variation of the momentum for both algorithms are identical. Of course, the same procedure can be repeated for all the first and second moments of all the increments of the variables in a time-step. Thus, despite the fact that the macroscopic properties of both algorithms are the same, it should be emphasised that the present algorithm preserves energy conservation at every time-step while all the other possible algorithms only do so in the mean. This can be verified by summing all the contributions to the energy for a pair of particles in a time-step. This point is of crucial importance when analysing the dynamic behaviour of the system, in particular when the exact conservation of the energy is checked during the simulations.

Regarding the second major point, we have emphasized in this article the existing tight relation between the overall properties of the DPDE model developed here and the macroscopic properties of real systems. This tight relationship will allow DPDE models to simulate the dynamic behaviour of real fluids, with respect to the equilibrium and transport properties of both momentum and energy. When the energy conservation is introduced, the existence of a *Thermodynamic behaviour* of the DPDE system becomes apparent. We have seen that the hypothesis leading to the present algorithm can reproduce not only the Maxwell-Boltzmann probability distribution for the momenta, but also the arbitrary probability distribution for the particle's internal energy. Furthermore, we have introduced a free energy from a partition function related to the system probability distribution. In the calculation of this partition function, the particle's internal energy  $u_i$  has been considered as an additional microscopic degree of freedom. From this formulation, we can obtain equations of state in terms of the parameters of the model. In particular, we have obtained a relationship between the internal energy of the whole system and its macroscopic temperature. This equation of state is useful since it allows one to relate the total energy introduced in a closed DPDE system with the final equilibrium temperature. The agreement between the predicted temperature and the simulated one is excellent. The pressure equation for this system has also been obtained, showing once more excellent agreement between the simulated and theoretical pre-

dictions. The pressure in a DPD system in general is constrained by the particle number density, which is much smaller than that of the corresponding real system being modelled. This is due to the implicit coarse-graining in the model, in which a packet of physical molecules is represented by a single DPD particle. Clearly, this is an area that needs to be further studied. However, for low Mach number flows, the DPDE fluid can be regarded as effectively incompressible, and thus a Boussinesq-like approximation is of use. Under these conditions, the thermal dilatation coefficient is the one that has to be properly modelled. In the particular system analyzed here, for instance, this coefficient,  $\alpha$ , is that of an ideal gas

$$\alpha \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{1}{T} \quad (4.2)$$

With a proper choice of the interaction potential this coefficient could be tuned according to the kind of fluid to be modelled. Note the excellent qualitative agreement found between the non-equilibrium simulations of a convective flow presented here and real fluid flows under equivalent conditions. These simulations can be theoretically analysed in light of the Boussinesq approximation. Finally, we have also identified a non-equilibrium free energy which acts as a Lyapunov functional for the dynamics of the system. Therefore, as seen in the simulations the DPDE system has an inherent irreversible tendency towards a thermal equilibrium when no external forcing exists. Moreover, other quantities have been theoretically derived such as the viscosity, the thermal conductivity, and the speed of sound. An in depth analysis of the derivation of these quantities and the consequences that can be drawn from its dynamic behaviour lie beyond the scope of the present work.

Therefore, the inclusion of the internal energy in the DPD algorithm reinforces the internal consistency of the model and opens interesting perspectives aimed at the use of these models in the simulation of the macroscopic-mesoscopic behaviour of simple and complex fluids.

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## References

- [1] P.J. Hoogerbrugge and J.M.V.A. Koelman, *Europhys. Lett.*, 1992, **19**, 155.
- [2] J.J. Monaghan, *Computer Physics Reports*, 1985, **3**, 71.
- [3] U. Frisch, B. Hasslacher, and Y. Pomeau, *Phys. Rev. Lett.*, 1986, **56**, 1505.
- [4] A. J. C. Ladd, *J. Fluid Mech.*, 1994, **271**, 285.
- [5] P. Español, P. Warren, *Europhys. Lett.*, 1995, **30**, 191.
- [6] C. Marsh, G. Backx, and M. H. Ernst, *Phys. Rev. E*, 1997, **56**, 1676.
- [7] E.S. Boek, P.V. Coveney, H.N.W. Lekkerkerker, and P. van der Schoot, *Phys. Rev. E*, 1997, **55**, 3124.
- [8] R.D. Groot and T.J. Madden, *J. Chem. Phys.*, 1998, **108**, 8713.
- [9] P.V. Coveney and K.E. Novik, *Phys. Rev. E*, 1996, **54**, 5134.
- [10] S. R. de Groot and P. Mazur, in *Non-equilibrium Thermodynamics*, Dover, New York, 1984.
- [11] W. van Saarloos, D. Bedeaux and P. Mazur, *Physica*, 1982, **110A**, 147.
- [12] L.D. Landau, and E. Lifshitz, *Fluid Mechanics*, Pergamon, New York, 1984.
- [13] H.B. Callen, *Thermodynamics and an Introduction to Thermostatistics*, John Wiley & Sons, New York, 1985.

- [14] J.B. Avalos and I. Pagonabarraga, *Phys. Rev. E*, 1995, **52**, 5881.
- [15] P. Mazur, D. Bedeaux, *Physica*, 1991, **173A**, 155.
- [16] N.G. van Kampen, *Stochastic Processes in Physics and Chemistry*, 2nd. edition, North Holland, Amsterdam, 1992.
- [17] J.-P. Hansen and I.R. McDonald, *Theory of Simple Liquids*, Academic Press, London, 1986.
- [18] J.B. Avalos and A.D. Mackie, *Europhys. Lett.*, 1997, **40**, 141.
- [19] Compare, for instance, with eq. (2.5.14) of ref.[17].
- [20] J.B. Avalos, *Phys. Rev. E*, 1996, **54**, 3955.
- [21] J.B. Avalos, *Phys. Rev. E*, 1996, **54**, 3971.
- [22] The local equilibrium is the lowest order term in an expansion of the Fokker-Plank equations essentially in a parameter scaling as  $1/\text{friction}$  (See, for instance, ref.[16] and references there in). This expansion method applied to the calculation of transport equations in a particle suspension can be found in refs. [20, 21].
- [23] The requirement that the heat capacity of the particle must be larger than  $k$  is due to the fact that the mesoscopic random heat flow is modelled as a continuum process subject to Gaussian statistics. Thus, the probability that a given particle,  $i$  say, at a given instant of time randomly loses more energy than the actual value  $u_i$  is exponentially reduced if  $\phi > k$ . This is due to the fact that the characteristic particle internal energy is of the order of  $\phi T$  while fluctuations in the same variable are of the order of  $kT$ . Therefore, in general, the model is only able to deal with "classical" or "high temperature" situations, where the DPD particles have an average internal energy substantially larger than the thermal energy  $kT$ .
- [24] I. Pagonabarraga, M.H.J. Hagen and D. Frenkel, *Europhys. Lett.* 1998, **42**, 377.

- [25] The relation between the equations of motion for a given system and the detailed balance condition can be found, for instance, in §V.6 of reference[16].
- [26] M. Doi and S.F. Edwards, *The Theory of Polymer Dynamics*, Claredon Press, Oxford, 1986
- [27] J.B. Avalos, *On the dynamics of dilute polymer solutions*, Ph.D. thesis, University of Barcelona, Barcelona, November, 1992; I. Pagonabarraga and J.B. Avalos (unpublished results).



## Figure Captions

Fig. 1: Equilibrium momentum probability distribution expressed in reduced variables, under the conditions ( $T^* = 1.1$ ,  $N = 30000$ ,  $C = 17$ ,  $B = 0.01$ ,  $r_\lambda = r_\zeta = 1.24$ ). The solid line stands for the theoretical prediction given in eq. (3.35) and the dots are simulation results. The time-step is  $\delta t^* = 0.01$ .

Fig. 2: Equilibrium particle's internal energy distribution expressed in reduced variables, under the conditions ( $T^* = 1.1$ ,  $N = 30000$ ,  $C = 17$ ,  $B = 0.01$ ,  $r_\lambda = r_\zeta = 1.24$ ). The solid line is a plot of the theoretical distribution given in eq. (3.36). The time-step used in this simulation is  $\delta t^* = 0.0001$ .

Fig. 3: Equilibration of the temperature starting from a random configuration under the same conditions as given in Fig. 1.

Fig. 4: Velocity field for a system under a temperature gradient orthogonal to a gravity field. The wall temperatures were chosen to be  $T_h^* = 2.8$ , on the left hand side, and  $T_c^* = 0.8$  on the right. The gravity field was  $g^* = 0.01$ , directed downwards. The system contains  $N = 100000$  particles in a cubic box of side  $N^{1/3}$ , with adiabatic walls in the top and the bottom sides of the cube and periodic boundary conditions in the remaining direction. The additional parameters were chosen  $B = 0.1$ ,  $C = 0.001$ ,  $r_\zeta = r_\lambda = 2$ , with a time-step  $\delta t^* = 0.01$ .

Fig. 5: Isothermal lines for the system described in Fig. 4. The numbers stand for the thermodynamic temperature  $T^*$  for a given line.

Fig. 6: Constant density lines for the system described in Fig. 3. The numbers represent the values of the density  $\rho^*$  for a given line. The distortion near the walls are caused by repulsive potentials exerted by the walls used to confine the system.











